Characterization and Mechanical Properties of Prepolymer and Polyurethane Block Copolymer with a Shape Memory Effect

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Abstract: The prepolymer and the final polyurethane (PU) block copolymer were synthesized by reacting 4,4-methylene bis(phenylisocyanate) with poly(tetramethylene glycol) and the prepolymer with 1,4-butanediol as a chain extender, respectively, to investigate the relation between phase separation and it's resulting properties. According to FT-IR data, the phase separation of hard and soft segments in the prepolymer and the PU block copolymer grew bigger by increasing the hard segment content, and the PU showed more dominant phase separation than the prepolymer. The heat of fusion due to soft segments decreased in both the prepolymer and the PU by increasing the hard segment content, whereas the heat of fusion due to hard segments increased in the PU did not appear in the prepolymers. The breaking stress and modulus of the prepolymer increased by increasing the hard segment content, and the elongation at break decreased gradually, and the PU showed the highest breaking stress and modulus at 58 % hard segment content. However, the best shape recovery of the PU was obtained at 47 % hard segment content due to the existence of proper interaction among the hard segments for shape memory effect. Consequently, the mechanical properties and shape memory effect of the PU were influenced by the degree of phase separation, depending on the incorporation of chain extender as well as the hard segment content.

Keywords: Polyurethane, Phase separation, Mechanical properties, Shape memory

Introduction

Thermoplastic polyurethane (PU) is, basically, a segmented multiblock copolymer whose chain structure is characterized by the alternating sequences of hard and soft segments. The hard segments form the physical crosslinks through polar interaction, hydrogen bonding, and crystallization, and the soft segments form the reversible phase due to the molecular motion in a rubbery state. The phase-separated structure gives the excellent elastomeric properties to the PU. Thus the PU has been widely applied in such various fields as elastomers, textiles, adhesives, coating materials, and biomedical materials. Recently, shape memory effect has been interestingly reported in this PU [1,2]. Reversible phase transformation of soft segment is reported to be responsible for the shape memory effect, which can be controlled via molecular weight of soft segment, mole ratio between hard and soft segments, the polymerization method, and the processing condition [3-5].

The PU is usually prepared by using one-step process or prepolymerization process. The latter method may result in the uniform hard segments in size [5], whereas the former method results in the somewhat inferior properties due to the decrease in effectiveness of hydrogen bonding. Since the segment arrangement and its phase-separated structure due to a combination of three compounds have a dominant influence on the properties of the final PU, the understanding

of the structure development and properties in prepolymer and PU is important. However, though many papers have been devoted to PU studies, the understanding of the relationship between the properties of prepolymers and PUs is still not entirely satisfied. According to Sanchez-Adsuar *et al.* [6-8], the properties of the prepolymer determine the properties of the final PU block copolymer such as adhesion properties when the amount of hard segments is small, and the chain extension step determines the PU block copolymer structure and properties when the amounts of hard segment is high. A synthesis method of urethane oligomers as an intermediate product for understanding the prepolymer properties has been also suggested [9].

In this paper, the phase separation, mechanical properties and shape memory effect of PU block copolymers were investigated with some characteristics of prepolymers.

Experimental

Materials and Polymerization

4,4-methylene bis(phenylisocyanate) (MDI, Junsei Chemical) and poly(tetramethylene glycol) (PTMG) (MW=1800 g/mol) were dried in a vacuum oven before use, and 1,4-butanediol (BD, Duksan Chemical) was stored on a 4 Å molecular sieve. Synthesis was carried out in two-step process via prepolymerization. In a 500 m*l* four-neck cylindrical vessel equipped with a mechanical stirrer, an appropriate amount of MDI and PTMG in 100 m*l* of dimethylacetamide (DMAC) which was freshly distilled before use were stirred under nitrogen at

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Table 1. Composition of prepolymer and PU synthesized in this study

| Sample code	Mole ratio			Wt% of hard segments
	MDI	PTMG	BD	
PR33	4.0	1	0	
PR41	5.5	1	0	
PR53	8.5	1	0	
PR62	13.0	1	0	62
PU47	5.5	1	4.5	47
PU58	8.5	1	7.5	58
PU68	13.0	1	12	68

80 °C for 3 hours to make the prepolymer. In the next, BD was added dropwise to the reaction mixture according to the MDI/PTMG ratios, and the remaining isocyanate group was intermittently checked by di-*n*-butylamine back-titration during polymerization to determine the progress of polymerization. After the polymerization was over, the PU was removed of solvent under vacuum and further solidified by storing in an oven (100 °C) for 24 hours. Table 1 represents some specifications of the prepolymer and the PU samples prepared. A number in sample code denotes MDI content or hard segment content by weight percentage.

Measurements

Fourier transform infrared(FT-IR) spectroscopic measurements of the PU films were performed using Jasco FT-IR 300E with an attenuated total reflectance method. Wide-angle x-ray diffractograms were obtained with a Rigaku Rint 2100 series x-ray diffractometer, using CuKα radiation at a scan rate of 5 °C/min. Differential scanning calorimetry (DSC) measurements were carried out with a TA instrument 2010 DSC (Du Pont). Samples were heated from room temperature at a rate of 10 °C/min in a nitrogen atmosphere.

The PU block copolymers were molded into tensile specimens with 3 mm thickness at 160-230 °C depending on the hard and soft segment content, and the freshly prepared PU specimens were immediately used for tensile test. A tensile test was performed at room temperature using a tensile tester (UTM Lloyd LR50K) with a dumbbell-type specimen, and the gauge length and crosshead speed were 25 mm and 10 mm/min, respectively.

To obtain the shape memory effect of the PU block copolymer, thermomechanical measurements were performed by analyzing the relationship between stress and strain at various temperatures, using a UTM equipped with a controlled thermal chamber. Firstly, deformation up to 50 % elongation was applied to the sample with a constant crosshead speed of 10 mm/min at 30 °C, which is near 20 °C above glass transition temperature (T_g), and then the sample was cooled to −10 °C, which is near 20 °C below T_g, with the 50 % elongation. After keeping at that temperature for 5 min with removal of
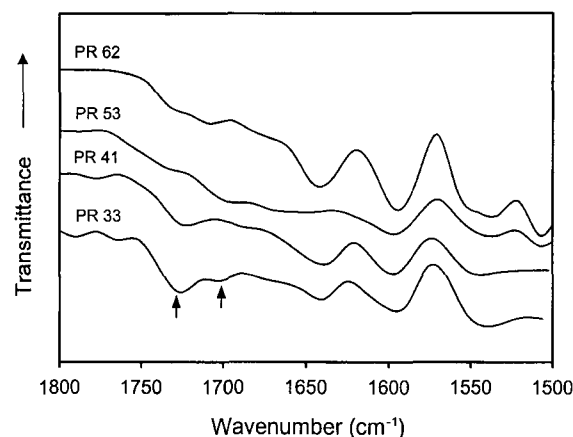
Figure 1. FT-IR spectra of prepolymers with different hard segment content.

the load, the recovery strain was measured by heating to 20 °C above T_g and then the shape recovery was calculated as the equations (1) and (2).

Shape retention (%) = (retention strain at T_g − 20)
×100/(strain at 50 % elongation)   (1)

Shape recovery (%) = (retention strain at 50 % elongation − recovery strain) × 100/(retention strain)   (2)

Results and Discussion

Figure 1 shows FT-IR spectra of prepolymer in a range of 1500-1800 cm^{-1} with different hard segment content. Two characteristic peaks near 1700 cm^{-1} and 1730 cm^{-1} are known to be ascribed to the stretching vibration of carbonyl(-C=O) group in hard segments [10-12]. The former peak is due to the presence of hydrogen bonded carbonyl group formed by phase separation and intermolecular interaction with -NH in hard segments, whereas the latter peak is due to the presence of non-hydrogen bonded carbonyl group due to dissolving in the matrix of soft segments. Strong interaction among hard segments leads to phase separation or domain formation, which is quite desirable in the point of shape memory effect. As the hard segment content increases, the FT-IR peak at 1700 cm^{-1} is growing bigger and that at 1730 cm^{-1} is getting smaller. It indicates that the phase separation of the prepolymer gradually and increasingly developed by increasing the hard segment content. A similar trend is also seen in the FT-IR spectra of the PU (Figure 2). Particularly, Figure 2 shows dominantly high peak intensity near 1700 cm^{-1} and weak peak intensity near 1730 cm^{-1} at the hard segment content similar to the prepolymer. That is, the phase separation occurs more dominantly in the PU than in the prepolymer, which reflects the increase of interaction among the hard segments due to an incorporation of BD.
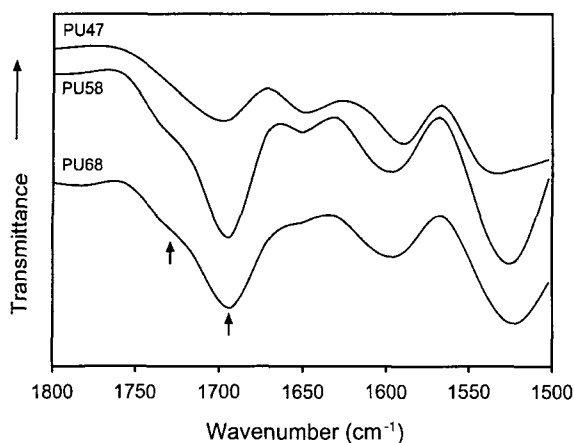
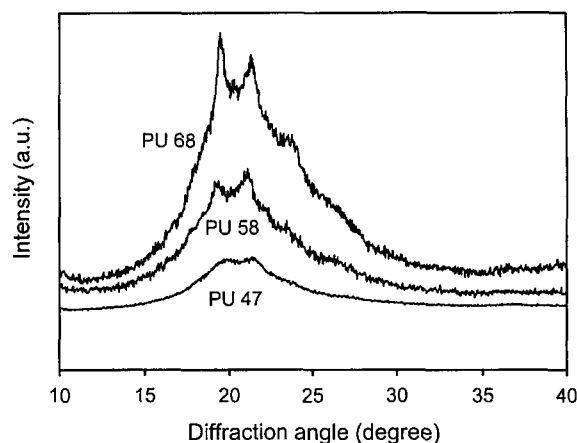**Figure 2.** FT-IR spectra of PU block copolymers with different hard segment content.

Figure 4. X-ray diffractograms of PU block copolymers with different hard segment content.
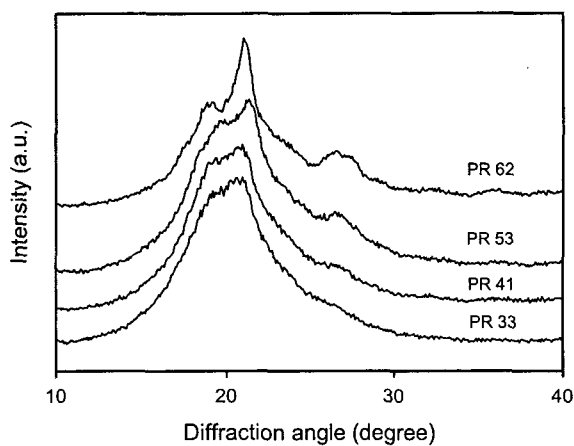

Figure 3. X-ray diffractograms of prepolymers with different hard segment content.

Figure 5. DSC heating thermograms of prepolymers with different hard segment content.

Figure 3 shows the x-ray diffractograms of prepolymers with different hard segment content. PR33 exhibits a small diffraction intensity around $2\theta = 18^{\circ}$ and 22°, indicating a presence of low crystallinity. However, as the hard segment content in the prepolymer increases, their peak intensity continues to increase gradually with a broad diffraction peak around $2\theta = 27^{\circ}$. In particular, PR62 exhibits quite a sharp diffraction peak. It is ascribed to the crystallization of hard segments due to the phase separation between hard and soft segments [13]. Similar results are shown in the diffraction curves of the PU as shown in Figure 4, and in particular quite strong intensities appear in PU68. It indicates that the increased interaction among hard segments after phase separation promotes the crystallization of hard segments.

Figure 5 shows the DSC heating curves of prepolymers with different hard segment content. By increasing the hard segment content, the endothermic peak near 25 °C due to soft segment melting decreases only slightly, and the heat of
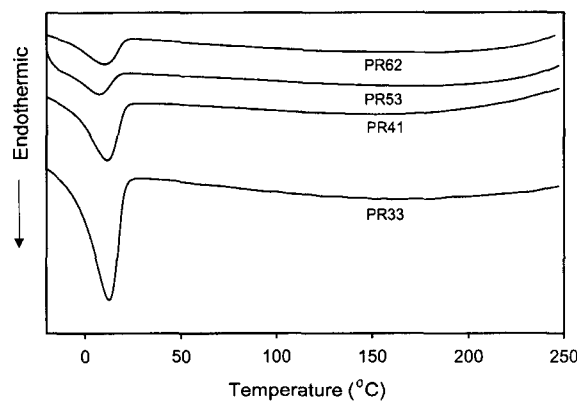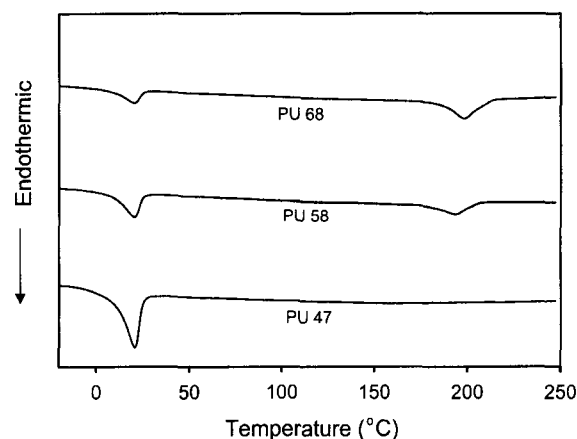

Figure 6. DSC heating thermograms of PU block copolymers with different hard segment content.

fusion declined gradually [14]. It indicates that the crystallinity of the soft segments is in inverse proportion to the hard

segment content. In other words, the ability of crystallization for the soft segments is weakened seriously as the hard segment content increases. However, no melting peak due to hard segments is seen in the prepolymer samples, which is maybe due to incomplete formation of hard segment domain in spite of increase of MDI content. In DSC results of PU block copolymers as shown in Figure 6, the melting peaks due to hard segments begin to appear when the hard segment content is 58 % or more. We can see easily from Figure 6 that the heat of fusion of the PU near 20 °C due to soft segment domain is getting smaller with increasing the hard segment content, whereas the endothermic peak due to the hard segments around 200 °C is growing bigger. These changes in melting behavior of the PU are ascribed to the increase of chain extender BD. That is, BD plays a role of inducing crystallization of hard segments due to the increased interaction among hard segments.

Figure 7 shows the tensile modulus of the prepolymer with different hard segment content. As the hard segment content
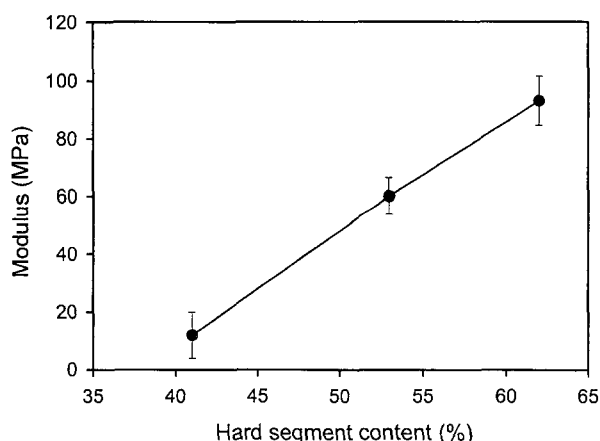
increases, the modulus exhibits a linearly increasing trend, which is due to the increase of hard domain resulting from intermolecular hydrogen bonding between the hard segments. That is, the rigid diphenylmethylene moiety coupled with hydrogen bonding and dipole-dipole interaction makes the PU very difficult to stretch as higher percentage of hard segment is incorporated [15]. Figure 8 shows the breaking stress and elongation at break of prepolymer as a function of hard segment content. The elongation at break decreases initially and then does less with increasing the hard segment content, and the breaking stress increases largely in the range of the hard segment content of 40-50 %. However, as shown in Figure 9, the PU shows maximum modulus and breaking stress at 53 % hard segment content. The decrease in breaking stress and modulus of the PU above 58 % hard segment content is considered to be due to the incorporation of excess hard segments including BD. That is, the modulus increases almost linearly with hard segment content at low hard segment content due to the stiffness of the polymer chain resulting from the polymeric interactions, however, at high hard segment content, the rigidity of the PU block copolymer would not allow it to stretch long. Thus the very high degree of physical cross-linking at high percentage of hard segment is responsible for the PU break up at short elongation, leading to the decrease in breaking stress. It emphasizes that the hard segment content is so important in determining the tensile strength and modulus.

Figure 7. Modulus of prepolymer as a function of hard segment content.

Figure 9. Breaking stress and modulus of PU block copolymers as a function of hard segment content.

Table 2. The shape retention and shape recovery measured for the PUs at each hard segment content

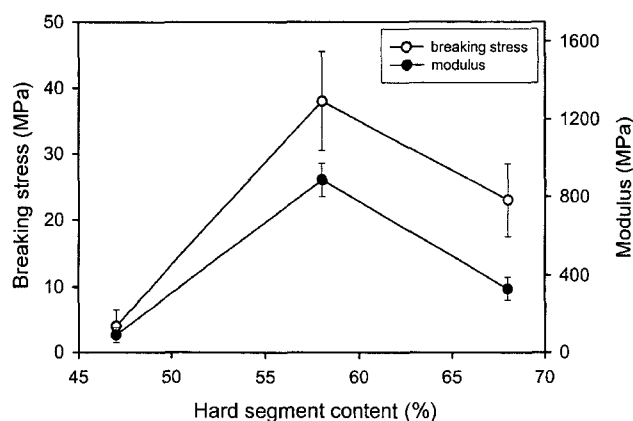| Hard segment content (%)	Shape retention (%)	Shape recovery (%)	Reference
30	90	83	15
47	93	95	this work
58	not available	not available	
68	not available	not available	

Figure 8. Elongation at break and breaking stress of prepolymers as a function of hard segment content.

Table 2 represents the shape retention of the PUs measured after it was deformed by 50 %, kept for 5 min at 20 °C below the glass transition temperature. The samples with 47 wt% of hard segment content showed the high shape retention of 93 %, however, the shape retention values for the samples with more than hard segment content of 50 wt% were not observed because their samples were not elongated enough to carry out the thermomechanical test. The shape recovery was measured after the sample was kept for 5 min at 20 °C above the glass transition temperature with the load removed. The good shape recovery of 95 % was obtained in the PU of 47 % hard segment content, which is ascribed that the PU can make strong interaction among hard segments enough to restore the polymer back to the original shape. When stress is applied to the PU, soft segment will be preferentially extended to the stress direction rather than hard segment due to the fact hard segment is close to glassy state and soft segment is rubbery at above the glass transition temperature. Stabilization of the PU through dipole-dipole interaction, hydrogen bonding, and induced dipole-dipole interaction of the hard segments is responsible for the high shape recovery at above the glass transition temperature. However, the shape recovery was not observed at PU58 and PU68 because it was not elongated enough due to the main chain rigidity of hard segments. According to our previous report [15], only the PU with hard segment content of 30 to 45 % could show high shape recovery of 80-95 %. Therefore, it can be concluded that the optimum hard segment content of the PU for application as shape memory materials is about 47 %, which was also associated with the mechanical properties due to phase separation between the hard and soft segments.

Conclusions

From investigating the structural characteristic of the prepolymer and PU block copolymer synthesized in a two-step process, the following conclusions could be obtained.

Phase separation of the prepolymer and PU developed increasingly with increasing hard segment content, based on FT-IR data and an incorporation of BD into the prepolymer induced the phase separation more dominantly. The heat of fusion due to soft segments in the prepolymer and PU decreased by increasing hard segment content, whereas that due to hard segments increased in the PU, however, did not appear in the prepolymers. The mechanical properties of prepolymers were linearly dependent on the hard segment content, whereas those of the PU showed the maximum value at 58 % hard segment content. However, the best shape recovery in the PU was obtained at 47 % hard segment content. Consequently, the mechanical properties and shape memory effect of the PU were greatly influenced by the degree of phase separation, depending on the segment content and incorporation of chain extender.

Acknowledgement

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